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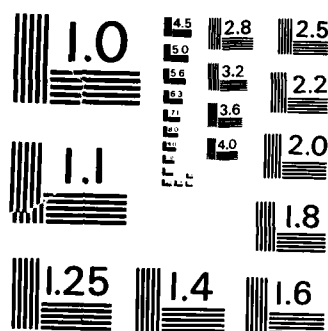
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K. J. Klabunde

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INTRODUCTION TO FREE ATOMS AND PARTICLES

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I. FREE ATOMS

The liberation of an atom from its elemental condensed form usually requires a great deal of energy. The atom thus formed, for example, a single atom of titanium (Ti), will be highly chemically reactive with added reagents. Of course, Ti atoms will also be very reactive with themselves, thus reforming titanium metal (or film).

The formation of free atoms can be carried out in a number of ways, all involving some high-temperature method in which the element is vaporized or a compound of the element is decomposed. These methods will be discussed in more detail later. At this point it is sufficient to say that over 90 of the elements can be treated in this way, that is, treatment with high temperature to form the atoms, which can then be used as chemical synthons or as building blocks for films.

II. FREE PARTICLES

Elemental solids are not the only sources of reactive, gaseous building blocks. High-temperature treatment of condensed molecular matter, such as metal oxides or sulfides, can often lead to gaseous coordination-deficient molecules, for example, titanium monoxide (TiO), which can be used as chemical synthons or as building blocks for films.

In theory the possibilities for generation of coordination-deficient reactive free particles are almost limitless. If two to four combined atoms make up the particle, almost all of the permutations of the elements must be considered: Ni_2 , TiO, Ti_3 , TiS, MoO_3 , B_2 , BSi_2 , SiC, RuC, PtTi, etc. In practice, *current* experimental methods limit the possibilities to hundreds (rather than thousands) of combinations.

To summarize, a free atom is a single, isolated reactive atom in a condensed inert matrix or in the gas phase. A free particle is a reactive coordination-deficient molecule of two to four atoms. These species are almost always formed by a high-temperature/energy process of one kind or another.

III. THE ELEMENTS

Figure 1.1 shows a periodic chart listing heats of formation of the elements [1, 2], which clearly points out that almost all of the elements exist as very stable condensed solids. The exceptions are the diatomic gases (H_2 , O_2 , N_2 , F_2 , Cl_2 , Br_2), the nonreactive atoms (He, Ne, Ar, Kr, Xe, Ra), and the liquids (Hg , Br_2).

Nearly all of the solid elements vaporize monatomically. The most notable exception is carbon where C_1 , C_2 , C_3 , and C_4 are formed, the

	H	Li	Be												B	(C)	N	O	F	Ne
kcal	52	39	78												134	171	113	59	19	0
		Na	Mg												Al	Si	(P)	(S)	Cl	Ar
kcal		26	35												78	107	79	67	29	0
		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	(As)	(Se)	Br	Kr	
kcal		21	42	82	113	123	95	67	100	101	103	80	31	69	69	72	54	27	0	
		Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	(Sn)	(Sb)	(Te)	I	Xe	
kcal		20	39	86	145	172	159	(155)	155	133	89	68	27	58	72	63	47	25	0	
		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
kcal		19	42	104	145	187	202	186	187	160	135	88	15	43	47	50	34		0	
		Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
kcal		97	85	77	50	43	82	87	71	75	75	56	40	102						
		Th	U																	
kcal		135	117																	

Fig. 1.1. Periodic chart showing heats of formation of the elements (kilocalories per mole). Those elements that yield polyatomics on vaporization of the bulk solid element are circled.

TABLE 1.1
Solid Elements^a with Physical Properties and Vapor Species^b

Element	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum (°C at about 10 μ pressure)	Vaporization method	Vapor composition
Li	180	1347	535	Resistive heating	Li
Na	98	883	289	Resistive heating	Na
K	64	774	208	Resistive heating	K, K ₂ (small)
Rb	39	688	173	Resistive heating	Rb
Cs	28	678	145	Resistive heating	Cs
Be	1278	2970	1225	Resistive heating	Be, Be ₂ (small)
Mg	649	1090	439	Resistive heating, arc, e-beam	Mg
Ca	839	1484	597	Resistive heating, arc, e-beam	Ca
Sr	769	1384	537	Resistive heating, arc, e-beam	Sr
Ba	725	1640	610	Resistive heating, arc, e-beam	Ba
Sc	1541	2831	—	Arc	Sc
Ti	1660	3287	—	Laser, e-beam, arc	Ti
V	1890	3380	—	E-beam, arc	V
Cr	1857	2672	—	Resistive heating, laser, e-beam, arc	Cr
Mn	1244	1962	—	Arc, resistive heating, levitation	Mn
Y	1552	3338	—	Arc	Y
Zr	1852	4377	—	Laser, e-beam, arc, sublimation by resistive heating	Zr
Nb	2468	4742	—	E-beam, arc	Nb
Mo	2617	4612	—	Laser, e-beam, arc, sublimation by resistive heating	Mo
Hf	2227	4602	—	E-beam	Hf
Ta	2996	5425	—	Laser, e-beam, arc	Ta

(continues)

TABLE 1.1 (continued)

Element	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum (°C at about 10 μ pressure)	Vaporization method	Vapor composition
W	3410	5660		Laser, e-beam, arc, sublimation by resistive heating	W
Re	3180			E-beam, arc sublimation by resistive heating	Re
Fe	1535	2750	—	Laser, e-beam induction, resistive heating	Fe
Ru	2310	3900	—	Resistive heating	Ru
Os	3045	5020	—		Os
Co	1495	2870	—	E-beam, induction, arc, resistive heating	Co
Rh	1966	3727		Arc, resistive heating, e-beam	Rh
Ir	2410	4130	—	E-beam, arc	Ir
Ni	1453	2732	—	Laser, e-beam, induction, arc, resistive heating	Ni
Pd	1552	3140	—	Arc, resistive heating	Pd
Pt	1772	3827	—	E-beam, resistive heating	Pt
Cu	1083	2567	—	E-beam, discharge, induction, laser, resistive heating	Cu Cu ₂ (0.0009)
Ag	961	2212	—	E-beam, induction, arc, resistive heating	Ag Ag ₂ (0.0005)
Au	1064	2807	—	E-beam, arc, resistive heating	Au Au ₂ (0.0007)

TABLE 1.1 (continued)

Element	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum (°C at about 10 μ pressure)	Vaporization method	Vapor composition
Zn	420	907	—	E-beam, arc laser, resistive heating	Zn
Cd	321	765	—	Arc, resistive heating, laser	Cd
Hg	-39	357	—	Arc, resistive, heating	Hg
B	2300	2550	—	E-beam, DC arc, induction, laser, resistive heating of C crucible	B, B ₂
Al	660	2467	—	Laser, resistive heating from BN or TiB ₂ or C crucible, e-beam, levitation	Al
Ga	30	2403	—	Resistive heating	Ga, Ga ₂ (small)
In	156	2080	—	Resistive heating	In, In ₂ (small)
Tl	304	1457	—	Resistive heating	Tl, Tl ₂ (small)
C	3632	4827	—	Sublimation by resistive heating, arc, laser	C, C ₂ , C ₃ , C ₄ , C ₅
Si	1410	2355	—	E-beam, laser levitation, resistive heating of Si rod	Si
Ge	937	2830	—	Resistive heating, laser	Ge
Sn	232	2260	—	Resistive heating, laser, e-beam	Sn, Sn ₂ , Sn ₃ , Sn ₄
Pb	328	1740	—	Resistive heating, laser, e-beam	Pb
As	817	613 (subl)	—	Resistive heating	As, As ₄ , As ₈
Sb	631	1750	—	Resistive heating, e-beam, laser	Sb ₃

(continues)

TABLE 1.1 (continued)

Element	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum (°C at about 10 μ pressure)	Vaporization method	Vapor composition
Bi	271	1560	—	Laser, resistive heating	Bi, Bi ₂ , Bi ₄
Se	217	685	—	Resistive heating, laser	Se ₂ -Se ₈
Te	452	1390	—	Resistive heating, laser	Te _s
La	921	3457	—	Resistive heating	La
Ce	799	3426	—	Resistive heating	Ce
Pr	931	3512	—	Resistive heating	Pr
Nd	1021	3068	—	Resistive heating	Nd
Pm	—	—	—		
Sm	1077	1791	650-900	Resistive heating	Sm
Eu	822	1597	—	Resistive heating	Eu
Gd	1313	3266	—	Resistive heating	Gd
Tb	1360	3123	—	Resistive heating	Tb
Dy	1412	2562	—	Resistive heating	Dy
Ho	1474	2695	—	Resistive heating	Ho
Er	1529	2863	—	Resistive heating	Er
Tm	1545	1947	—	Resistive heating	Tm
Yb	819	1194	500-650	Resistive heating	Yb
Lu	1663	3395	—	Resistive heating	Lu
Th	—	—	—		
Pa	< 1600	—	—		
U	1132	3818	—	Resistive heating, e-beam	U
Np	640	3902	—		
Pu	641	3232	—		
Am	994	2607	—		

^a Arranged by families of elements in the periodic table moving from left to right.

^b Taken mainly from Klabunde [1].

^c Atmospheric pressure.

proportion of which depends on the method of graphite vaporization. A few other elements behave similarly, and Table 1.1 lists the polyatomics observed for these materials.

Table 1.1 also lists the melting points, boiling points (atmospheric pressure), and temperatures at which the vapor pressure of the element is 1×10^{-2} torr [3], which is an estimate of the temperature at which convenient vaporization under vacuum occurs. Listed also are the most commonly used methods of vaporization of each of the elements. These high-temperature techniques are discussed in more detail later in this chapter.

It should be emphatically stated here that a great deal of additional work is needed on determining vapor compositions. Most of the data listed are based on Knutsen cell/mass spectrometry experiments, which are fine for systems at thermal equilibrium. However, synthetic applications of high-temperature species requires vaporization from an open crucible or hearth, and the vapor compositions for many of the elements may be quite different under these conditions.

IV. MOLECULAR SOLIDS

Synthetic and natural molecular solids exist everywhere. These include the metal oxides, metal sulfides, metal carbides, metal nitrides, metal phosphides, metal halides, and metal alloys. If ternary or quaternary compounds of the elements are considered a huge number of possible combinations exist.

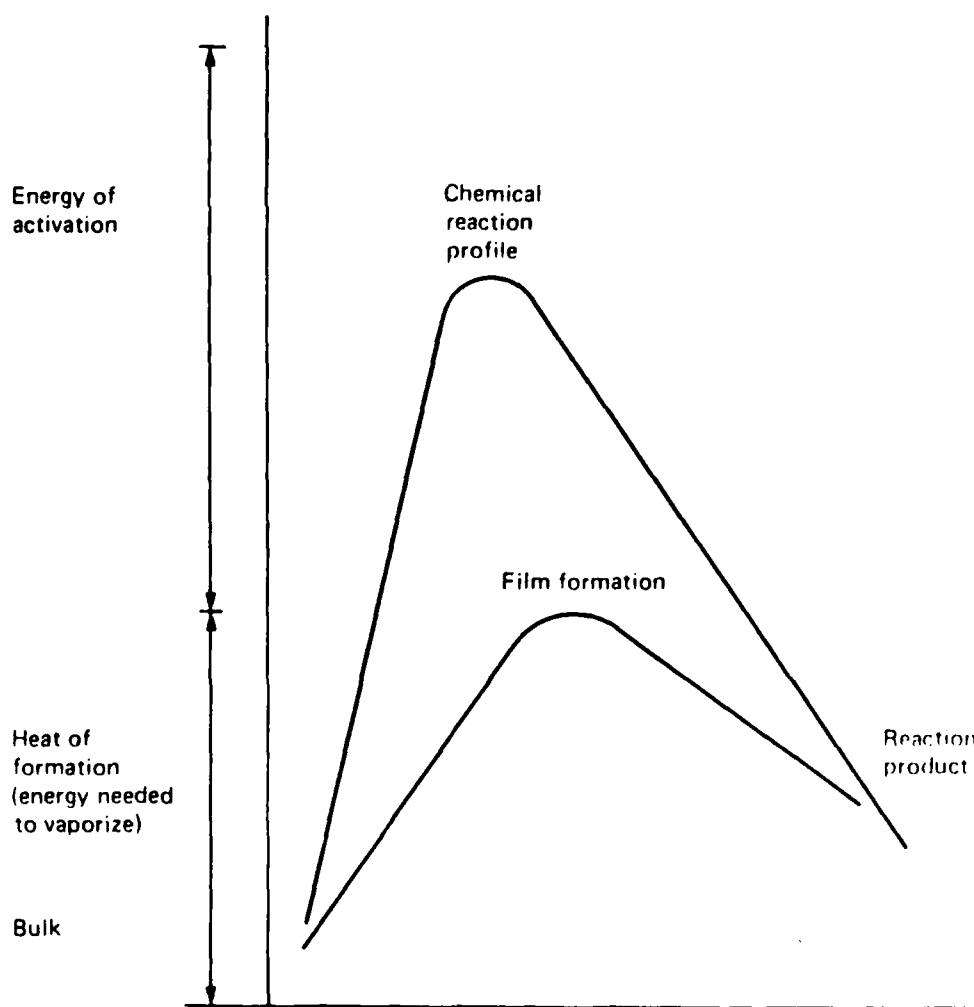


Fig. 1.2. Reaction coordinate for a free atom or particle

TABLE 1.2

Examples of Molecular Solids^a Studied under Vaporization Conditions^b

Substance	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum	Vapor species and comments
LiF	845	1676	1047	LiF, (LiF) ₂ (large)
NaCl	801	1413	865	NaCl, (NaCl) ₂ (large)
KBr	734	1435	795	KBr, (KBr) ₂
RbBr	693	1340	781	RbBr, (RbBr) ₂ (18% _n)
CsCl	645	1290	744	CsCl, (CsCl) ₂ (20% _n)
Li ₂ O	> 1700	1200	980	Li ₂ O
K ₂ O	d 350	—	450	K ₂ O, K, O ₂
BeF ₂	—	—	500–1100	BeF ₂ , (BeF ₂) ₂ (1% _n)
BeBr ₂	490	520	—	BeBr ₂ , (BeBr ₂) ₂
MgBr ₂	711	—	570	MgBr ₂ , (MgBr ₂) ₂ (1% _n)
SrO	2430	3000	1400–1500	SrO, Sr (trace)
ScF ₃	—	—	—	ScF ₃ (D _{3h} geometry)
ScCl ₃	939	—	—	ScCl ₃ , (ScCl ₃) ₂
TiCl ₄	– 25	136	—	TiCl ₄ , (TiCl ₄) ₂
TiO ₂	1830	2500–3000	—	Ti ₃ O ₅ , Ti ₄ O ₇ , TiO, TiO ₂
TiO	1750	> 3000	—	TiO (mainly), Ti ₂ O, Ti ₂ O ₃ , Ti ₃ O ₅ , Ti ₄ O ₇ , Ti ₅ O ₉ , Ti ₁₀ O ₁₉ , TiO ₂ , Ti
TiS	—	—	1900	TiS, Ti, S ₂ , S
VCl ₄	– 28	149	—	VCl ₄
VS	d	—	—	VS, V, S
MnF ₂	856	—	—	MnF ₂ , Mn ₂ F ₄
MnF ₃	d	—	—	MnF ₃ , Mn ₂ F ₄
YF ₃	1387	—	—	YF ₃ (C _{3v} geometry), YF ₂ (C _{2v} geometry)
YO	2410	—	—	YO
ZrF ₄	—	subl 903	600	ZrF ₂ , ZrF ₃ , ZrF ₄
ZrO ₂	2700	5000	—	ZrO, ZrO ₂
ZrS ₂	1550	—	1400	Zr ₂ S ₄ , S ₂
NbF ₅	72	236	—	Nb ₃ F ₁₄ , NbF ₄
NbO	—	—	1630	Nb, NbO, NbO ₂
MoO ₃	795	subl 1155	—	Mo ₃ O ₆ , Mo ₄ O ₁₂ , Mo ₅ O ₁₅
MoS ₂	1185	subl 450	—	S ₂
WO ₃	1473	—	—	W ₃ O ₉
ReO ₂	d 1000	vap 350	—	Re ₂ O ₇ , ReO ₃ , HReO ₄
ReO ₃	—	vap 750	—	Re ₂ O ₇ , ReO ₃ , HReO ₄
FeBr ₂	d 684	—	—	FeBr ₂ , (FeBr ₂) ₂
FeI ₂	red heat	—	—	FeI ₂ , (FeI ₂) ₂
Fe ₂ O ₃	1565	—	—	O ₂ , lower oxides
CoCl ₂	724	1049	—	CoCl ₂ , (CoCl ₂) ₂
CoO	1935	—	—	Co, O ₂ , CoO

TABLE 1.2 (continued)

Substance	mp (°C)	bp' (°C)	Vaporization temperature under vacuum	Vapor species and comments
NiBr ₂	963	—	—	NiBr ₂ (linear)
RhO ₂	—	—	—	Rh, RhO, RhO ₂
PdBr ₂	d	—	—	(PdBr ₂) ₄ , (PdBr ₂) ₆
PdO	870	—	—	Pd, PdO
PtCl ₂	d 581	—	—	Pt ₄ Cl ₁₀ , Pt ₆ Cl ₁₂ , Pt ₄ Cl ₈
CuCl	430	1490	—	CuCl, Cu ₂ Cl ₂ , Cu ₄ Cl ₄
CuBr	492	1345	—	CuBr, Cu ₂ Br ₂ , Cu ₃ Br ₃
CuF ₂	d 950	—	—	CuF ₂
Cu ₂ O	1235	d 1800	—	Cu, Cu ₂ O, CuO
AgCl	455	1550	—	AgCl, Ag ₃ Cl ₂ , (AgCl) ₄
AgBr	432	1505	—	AgBr, (AgBr) ₄
AgI	558	1506	—	AgI, Ag ₃ I ₂ , I, I ₂
ZnBr ₂	394	650	—	ZnBr ₂
CdCl ₂	568	960	—	CdCl ₂ , (CdCl ₂) ₂
CdS	—	subl 980	—	Cd, S ₂
Hg ₂ Br ₂	236	318	—	Hg, HgBr ₂
HgO	d 500	—	—	Hg
BF	(BF ₃ + B at 2000°C →)	—	—	BF, BF ₄
BCl	(BCl ₃ + B at 1100°C →)	—	—	BCl, B ₂ Cl ₄ , BCl ₄
B ₂ O ₃	460	1860	—	B ₂ O ₃
BS ₂	—	—	550-1100	BS ₂ , (BS ₂) ₂ , (BS ₂) ₄
B ₂ S ₃	310	—	300-600	B ₂ S ₃ polymers, BS ₂ , B ₂ S ₂ , B ₆ S ₁₂ , B-S ₁₄
AlF	(AlF ₃ + Al at 800-1000°C →)	—	—	AlF, (AlF) ₂
Al ₂ O ₃	2020	2980	2000-4000	Al ₂ O ₃ , AlO, Al ₂ O, Al, O, O ₂
GaF	(CaF ₂ + Ga at 800-1300°C →)	—	—	GaF
Ga ₂ O	(Ga ₂ O ₃ + Ga →)	—	—	Ga ₂ O
Ga ₂ S ₃	1255	—	950	Ga ₄ S ₄ , S
GaAs	1238	—	700-900	Ga, As, As ₂ , As ₄
GaP	—	—	741-953	Ga, P ₂
InCl	225	608	—	InCl
In ₂ Cl ₃	—	641	340-450	InCl, InCl ₃
In ₂ O	(In ₂ O ₃ + In at 600-950°C →)	—	—	In ₂ O
TlF	327	826	—	TlF, Tl ₂ F ₂
Tl ₂ O	300	—	—	Tl ₂ O
CS ^d	-130	(CS ₂ $\xrightarrow{\text{discharge}}$)	—	CS, S, CS ₂
		several other methods have also been used		
SiF ₂	(SiF ₄ + Si at 1150°C →)	—	—	SiF ₂ , SiF ₄
GeF ₂	d 350	subl	—	GeF ₂ , (GeF ₂) ₂
GeO ₂	1115	—	—	GeO, GeO ₂ , O

(continues)

TABLE 1.2 (continued)

Substance	mp (°C)	bp ^c (°C)	Vaporization temperature under vacuum	Vapor species and comments
SnS	880	1230	1000–1200	SnS, (SnS) ₂
PbBr ₂	373	1166	530–660	PbBr ₂
PbO	888	1132	—	Pb ₄ O ₄ favored, Pb _n O _n , where <i>n</i> = 1–6
Sb ₂ O ₃	656	subl 1550	290–425	SbO, Sb ₂ O ₂ , Sb ₃ O ₃ , Sb ₄ O ₄ , Sb ₂ O ₄ , Sb ₂ O ₅ , Sb ₂ O ₆
Bi ₂ O ₃	820	1855	—	Bi ₄ O ₄ , Bi ₄ O ₅ , Bi ₃ O ₃ , Bi ₂ O ₂ , BiO, Bi, O ₂
TeO	d 370	—	—	Te, O ₂ , TeO
LaF ₃	—	—	—	LaF ₃ , La ₂ F ₆
YbCl ₂	702	1900	—	YbCl ₂
ThO ₂	3050	4400	1500–2000	
UO ₂	2500	subl 1400–2300	—	UO ₂ mainly, U, UO

^a Arranged by families of the periodic chart moving from left to right.

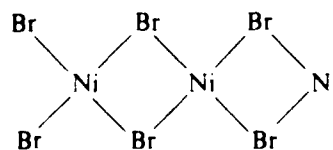
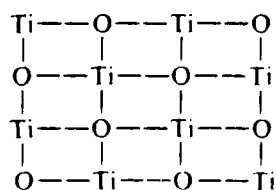
^b Taken mainly from Klabunde [1].

^c Atmospheric pressure.

^d See Klabunde *et al.* [5] for further reading on the synthetic chemistry of CS.

A severe limitation in the formation of free molecules (particles) from these solids is the fact that high-temperature vaporization often leads to decomposition/disproportionation. Thus, for example, sublimation of MoO₃ solid yields vapor species Mo₃O₉, Mo₄O₁₂, Mo₅O₁₅, and others. Also, HfS₂ yields Hf₂S₅ and S₂, while RhO₂ yields Rh atoms, RhO, and RhO₂ [1]. On the other hand, many molecular solids can be smoothly vaporized. For example, TiO yields mainly TiO vapor [4] and NiBr₂ yields NiBr₂ vapor. Summaries of these processes are available [1]. Still, a great deal needs to be done regarding vaporization of molecular solids; so much is still not known.

Of course the structure of the solid and the strength of the bonding determines the ease with which vaporization and/or decomposition can occur. Generally high-melting-point/high-boiling-point materials have some ionic bonding which must be broken up. Bridging bonds also need to be broken:



The reactivity of the resultant free particle TiO or NiBr_2 will depend on its readily available orbitals, low steric restrictions to reaction, and somewhat on the energy required to form it. Thus, TiO is difficult to form (vaporizes at $1700\text{--}2000^\circ\text{C}$ under vacuum; the free TiO molecules are extremely reactive), while NiBr_2 readily sublimates at several hundred degrees and the resultant NiBr_2 particles have less tendency to react with added reagents, and usually repolymerize to $(\text{NiBr}_2)_n$ film. The heat of formation (or energy to vaporize) is a potential energy that puts the particle higher on the energy/reaction coordinate for a chemical reaction (see Fig. 1.2).

Although a more thorough summary is available in an earlier book [1], Table 1.2 summarizes the physical properties of the most important solid substances that have been or could be vaporized and the resultant free particles used as synthons of new compounds or as building blocks for films.

V. EXPERIMENTAL METHODS

The development of high-temperature species as synthons and film precursors has been heavily dependent on the availability of excellent vacuum technology and on high-temperature ceramics. Industrial technology in these areas is highly developed and improving rapidly. Technology is available and is being used for vaporization of large quantities of metals, metal oxides, metal sulfides, and other substances [6]. Techniques will be dealt with in some detail in later chapters. A brief summary here may be helpful, however.

A. Resistive Heating Vaporization

Electrical resistive heating is commonly employed in industry and in the laboratory. Many different crucibles or vaporization sources are available commercially [7]. Usually a tungsten coil is coated with Al_2O_3 , and the resultant crucible is very useful for vaporizing Mn, Fe, Co, Ni, Pd, Cu, Ag, Au, Sn, Pb, NiCl_2 , and many other materials. Another variation is a tungsten coil wrapped around an Al_2O_3 cup, which serves well for low-temperature metals such as Mg, Ca, Zn, and others. Sometimes tungsten, molybdenum, or tantalum boats are used to vaporize metals directly, and these work well for Ti, V, and Cr vaporizations. The limitations are the temperatures Al_2O_3 can withstand ($\sim 2000^\circ\text{C}$) or that tungsten can withstand without alloying with the evaporant. Other variations exist where materials can be vaporized downwards continuously using a wire feed [7, 8].

B. Electron-Beam Vaporization

A beam of electrons can be focused on the sample, and by using voltage differences between the filament emitting the electrons and the water-cooled hearth holding the sample, electrons can be passed through it causing heating and eventual vaporization [9]. The main advantages of this method are that it can be scaled up readily and, more importantly, high-boiling metals such as Pt, Rh, Mo, W, and U can be vaporized without materials problems, since the hearth can be kept cool. Semiconductor substances such as YO, TiO, ThF₃, TaO, SrF₂, Nd₂O₃, and Nb₂O₅ can also be vaporized this way. Both magnetically and electrically focused beams can be fashioned. Also, positive filament or positive hearth (reversed polarity from normal) e-beams can be employed; the positive hearth type is more difficult to engineer but minimizes stray parasitic electrons and x rays.

C. Laser Evaporation

Many metal vaporization studies using a variety of lasers have appeared. Koerner von Gustorf [10] used YAG (yttrium aluminum garnet doped with Nd³⁺) lasers; CO₂ lasers are also usable but with less efficiency. Small-scale vaporizations can be done with ease and great control [11]. However, large-scale vaporizations are very destructive [12]. Two problems are encountered: molten metals behave as good mirrors for the laser beam and the window allowing the laser beam into the vacuum chamber can become coated with evaporant film. The advantages of laser evaporation are precise control of the vaporization "spot", continuous vaporization can be done either with a cw laser or with continuing laser bursts, and stray radiation is less of a problem than with electron beam methods.

D. Sputtering and Magnetron Sputtering

These methods will be covered in some detail later in this book. For the sake of definition, sputtering is vaporization of a material by bombarding it with high-energy atoms and ions of argon or other inert gases. The force of impact causes atoms or molecules to be ejected from the surface. Sputtering is very important in industry even though it has poor energy efficiency (5–10% compared with 35% for e-beams) [6]. Magnetron sputtering is dealt with in some detail in Chapter 7 and makes use of permanent magnets coupled with rf or dc sputtering.

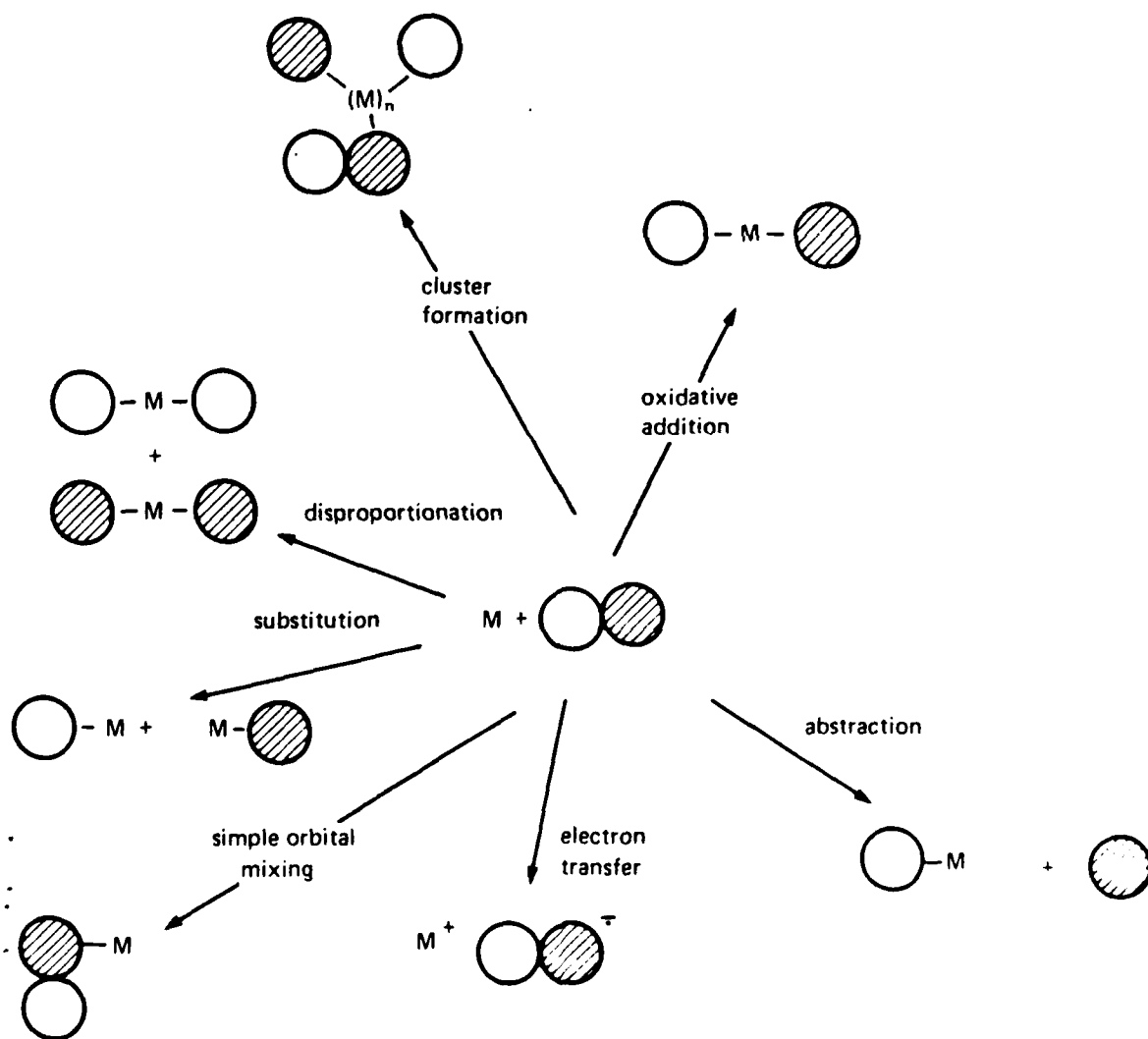
E. Induction Heating

By using a conducting coil surrounding the sample, a magnetic field can be set up such that electron current in the sample is induced, thereby heating

and eventually vaporizing the sample. Under some conditions the sample can even be levitated [13]. Induction heating is limited because of the coupling needed between the coil and the sample. When vacuum apparatus is required, it becomes difficult to position the coil and sample properly for effective coupling.

VI. USES OF FREE ATOMS AND PARTICLES IN CHEMICAL AND FILM-FORMATION PROCESSES

The high-temperature generation of free atoms and particles has been very useful in chemistry [1]. Low-temperature matrix isolation of these species for spectroscopic study has taught us a great deal about electronic states and



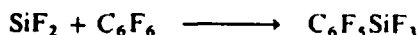
Scheme 1.1. Illustration of low-temperature reaction chemistry of free atoms; (M is a metal atom, and the open circles and cross-hatched circles are organic or inorganic molecules, respectively, with some functional group) [1, 7].

bonding in metal atoms, dimers, and trimers [14]. Particles such as metal halide molecules or fragments have also been frozen and spectroscopically analyzed [15]. Matrix isolation spectroscopy has also taught us much about the electronic/bonding properties of free atoms and particles. In Chapter 2 we will take a closer look at some of these studies.

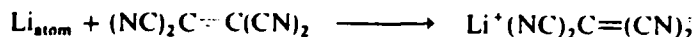
Reaction chemistry of free atoms and particles has been extremely fruitful and has made "vapor synthesis" or the "metal atom/vapor technique" an established synthetic method in inorganic and organometallic chemistry [1]. The high reactivity of free atoms and particles allows low-temperature reaction chemistry to proceed smoothly, and many unusual new compounds have been prepared by combining metal atoms with organic molecules. These studies have not only led to new molecules but have also contributed to a more fundamental understanding of metal-organic interactions, which of course is important in catalysis and other surface chemistry phenomena.

Basically the low-temperature reaction chemistry of free atoms and particles can be illustrated by Scheme 1.1. Some classic chemical reactions are shown below as examples [1]:

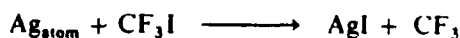
Oxidative addition:



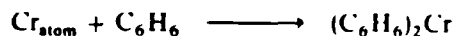
Electron transfer:



Abstraction:

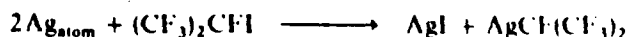


Simple orbital mixing:

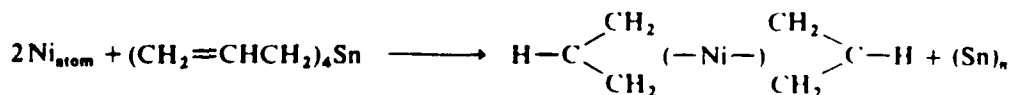


benzene sandwich compound

Substitution:



Disproportionation and ligand transfer:



Cluster formation [16]:



TABLE 1.3

Materials Normally Vaporized in Industry: Suggested Methods, Remarks, and Uses^a

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
Al	660		Res W boat or wire, boron nitride crucibles	Use stranded W wire, alloys W, corrodes Al_2O_3	Films on plastics and other materials
Al_2O_3	2050	2000	EB or sputtering Res W boat	Recommend rf sputtering	Protective anti-reflective coatings
Sb	630	—	Res alumina crucible, Mo, Ta boats	Toxic, use external heater	
Sb_2O_3	656	400-500	Res Pt		Multilayer coating
Sb_2S_3	550	300-500	Res Mo or Ta boats or wires	—	IR filters, photoconductors
As	814	—	Res alumina crucible	Sublimes, toxic use external heater	
B	2000	—	Res C boats or strips, EB		
Ba	717	—	Res Mo, Ta, W boats	Does not alloy	
Be	1284	—	Res W boat, EB	Alloys refractory metals, toxic	
Bi	271		Res alumina crucible	Toxic, use external heater	
Bi_2O_3	820	800-1000	Res Pt or alumina crucible	—	Heat-reflecting films support for Au films on glass
Cd	321	—	Res alumina crucible, Mo, Ta, W boats	Use external heater	
CdS	1750	600-800	Res Mo, Ta, or C boats	—	IR filters, multi-layer coatings, photoconductors, thin-film transistors

(continues)

TABLE 1.3 (continued)

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
CdSe	1350	500-700	Res Mo, Ta, or alumina crucible		IR filters, multi- layer coatings, photo- conductors, thin-film transistors
CdTe	1041	600-1000	Res Mo, Ta wires or boats		IR filters, multi- layer coatings, photo- conductors, thin-film transistors
Ca	810	—	Res alumina crucible	Use external heater	
CaF ₂	1360	1300-1500	Res Mo, Ta wire or boats		Multilayer coatings, insulating films in thin-layer circuits
C	3650	—	Carbon arc		
CeF ₃	1324	1200-1600	Res Mo, Ta, W wires or boats		Multilayer coatings
CeO ₂	1950	—	EB, Res W boats, or alumina crucible	EB best; reacts with refractory source	Multilayer coatings
CsI	621	600-800	Res Mo, Ta		X-ray fluorescent screens
Cr	1900	—	Res W boat		
CrO ₃	196	1900-2000	Res W		Absorbent brown films for optical glasses
Co	1478	—	Res alumina crucible		
Cb	2500	—	Res W boat		
Cu	1083	—	Res alumina crucible, Mo, Ta, W boats		
Ga	30	—	Res alumina crucible or coated boat	Use external heater	
GaP	1348	—	Res W boat		
Ge	959	—	Res alumina crucible, Mo, Ta, W boats		
GeO ₂	1115	—	Res Mo, Ta, W boats		

TABLE 1.3 (continued)

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
Au	1063	—	Res alumina crucible or coated boat	—	—
In	157	—	Res Mo, W boat	—	—
In ₂ O ₃	850 ^e	—	Res Pt wires	—	Transparent heating elements on glass
Fe	1535	—	Res alumina crucibles, W boats	Sputters well	—
Fe ₂ O ₃	1565	—	Res W boat	Reactively sputter	IR interference film and beam splitter
LaF ₃		1200–1600	Res Mo, Ta	—	Multilayer coatings
Pb	328	—	Res alumina crucible, Mo, W boats	Use external heater, toxic	—
PbF ₂	855	700–1000	Res Pt or alumina crucibles	—	Multilayer coatings
Li	179	—	Res Fe or quartz crucibles	Use external heater	—
LiF	870	800–1000	Res Mo, Ta EB	—	UV reflective films, multi- layer coatings
Mg	651	—	Res W boats or alumina crucible	Use external heater	—
MgF ₂	1395	—	Res Mo, W boats, C crucible	—	Antireflective films on glass, decorative coatings
MgO	2800	2000	EB	—	Multilayer coatings
Mn	1244	—	Res Mo, W boats or alumina crucible	—	—
Mo	2622	—	EB, Res Mo wire	Sputters well	—
Nd ₂ O ₃	—	1600–2000	EB, Res W	—	Multilayer coatings
Nd ₂ O ₃	1520	1400–1600	EB, Res W	—	Dielectric films, multilayer coatings

(continues)

TABLE 1.3 (continued)

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
Ni	1455	—	Res alumina crucible, W boats	Sputters very well	—
Ni/Cr	1360	—	Res alumina crucible, W boats	Deposits as chrome alloy	—
Pd	1555	—	Res alumina crucible, W boats	Alloys with refractory metals	—
Pt	1774	—	Res W filament or wire	Alloys and must be evaporated rapidly	—
Se	217	—	Res alumina crucible or W boat	Toxic	—
Se	1420	—	Res beryllium oxide or C crucible, EB	Can use rf sputtering	—
SiO ₂	1800	1600	EB	—	Laser coatings
SiO	—	1200–1600	Res Mo, Ta wires or boats	—	Antireflective films, protective dielectric films, decorative coatings, electron microscopy specimens
Ag	961	—	Res alumina boats, Ta, Mo boats	—	—
NaF	1040	1000–1400	Res Mo, Ta	—	Multilayer coatings
SrF ₂	1190	1000–1400	EB, Res W	—	Low index layers for IR films
Ta	2996	—	EB	Sputters well	—
Ta ₂ O ₅	1470 ^e	2000	EB	—	Dielectric films
Te	452	—	Res alumina crucible, W boat	Use external heater, toxic	—
Th	1827	—	Res W boat	Wets W	—
ThF ₄	—	1000–1200	Res Mo, Ta	—	Laser coatings, multilayer coatings

TABLE 1.3 (continued)

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
Ni	1455	—	Res alumina crucible, W boats	Sputters very well	—
Ni/Cr	1360	—	Res alumina crucible, W boats	Deposits as chrome alloy	—
Pd	1555	—	Res alumina crucible, W boats	Alloys with refractory metals	—
Pt	1774	—	Res W filament or wire	Alloys and must be evaporated rapidly	—
Se	217	—	Res alumina crucible or W boat	Toxic	—
Se	1420	—	Res beryllium oxide or C crucible, EB	Can use rf sputtering	—
SiO ₂	1800	1600	EB	—	Laser coatings
SiO	—	1200–1600	Res Mo, Ta wires or boats	—	Antireflective films, protective dielectric films, decorative coatings, electron microscopy specimens
Ag	961	—	Res alumina boats, Ta, Mo boats	—	—
NaF	1040	1000–1400	Res Mo, Ta	—	Multilayer coatings
SrF ₂	1190	1000–1400	EB, Res W	—	Low index layers for IR films
Ta	2996	—	EB	Sputters well	—
Ta ₂ O ₅	1470*	2000	EB	—	Dielectric films
Te	452	—	Res alumina crucible, W boat	Use external heater, toxic	—
Th	1827	—	Res W boat	Wets W	—
ThF ₄	—	1000–1200	Res Mo, Ta	—	Laser coatings, multilayer coatings

TABLE 1.3 (continued)

Material ^b	mp (°C)	Evaporation temperature	Evaporation method ^c	Remarks	Uses ^d
Sn	232	—	Res alumina crucible, Mo, Ta boats	—	Wets Mo
SnO ₂	1127 ^e	—	Res W boat	—	Antistatic coatings and transparent heating elements
Ti	1727	—	Res W boat, EB	Deposits contain traces of W	—
TiO ₂	1850	2200	EB	—	Multilayer and laser coatings
TiO	1750	1700–2000	EB, Res W	—	Antireflective films, decorative coatings, beam splitters
W	3382	—	Res W wire, EB	Sputters well	—
U	1132	—	EB, Res W wire or boat	Sputters well	—
V	1697	—	Res Mo, W boats	Evaporates just at molten state	—
Zn	419	—	Res alumina crucible	Use external heater	—
ZnS	1900	1000–1100	Res Mo, Ta or C crucible	—	Beam splitter, very hygroscopic
ZnSe	—	600–900	Res Mo, Ta	—	IR filters, color filters
Zr	2127	—	Res W	Deposits contain traces of W	—
ZrO ₂	2700	2500	EB	—	Antireflective films, multilayer coatings

^a From Klabunde [8]. Data for table originally from Feldman *et al.* [17], Baer [18], Adams [19], the Sylvania Emissive Products Catalog, and the Vacuum Evaporation Sources Catalog (published by R. D. Mathis Company).

^b Arranged alphabetically according to name of compound or element (approximately).

^c Res refers to resistive heating. Thus Res W would mean to vaporize the substance directly from a W wire, filament, or crucible. Res alumina crucible would mean an integral W Al₂O₃-coated crucible. However, if under Remarks it states to use an external heater would mean an alumina crucible placed in a W wire heater. EB means electron-beam vaporization works best.

^d Vapor-deposited metal films are generally used for decorative, protective, or electronics applications.

^e Decomposes.

This last process, cluster formation, is the precursor of film formation and will be examined in more detail in Chapter 2.

In the absence of some added reactant, condensation of free atoms and particles does not lead to new chemical compounds but instead to polymers/films. With the availability of excellent high-vacuum technology and high-temperature sources, industry has made great use of this process. Table 1.3 lists some of the materials normally vaporized industrially for film preparation [8].

Actually Table 1.3 is only a sampling. The possibilities for further production of films are staggering. Remember that with the availability of vacuum technology, high-temperature sources, electron beams, lasers, sputtering apparatus, and induction heating, experimental difficulties will be largely overcome. Our only limitations will be on synthesis of new vaporizable solids and applications of the resultant films.

In conclusion, the use of free atoms and particles for film formation could be exploited considerably more. The film-forming process (the polymerization of the reactive atom or particle) has a low activation energy and can be carried out at low temperature. However, controlling the polymerization to yield special films, perhaps epitaxial films, presents some problems. Thus, it is worthwhile to look in some detail at the embryonic stages of clustering of free atoms and particles. Chapter 2 deals with these topics.

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